UTILIZATION OF WASTE

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AN EFFICIENT TECHNOLOGY FOR PRODUCTION OF FAIENCE ARTICLES USING CALCIUM-CONTAINING WASTE

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The results of the study of the sintering specifics of ceramic mixtures using highly calciferous waste as a material component are discussed. It is found that for a certain ratio of alkaline and alkaline-earth components, the ceramic crock structure is represented by calcium silicates and aluminosilicates which ensure good service properties of the product.

One of the main lines of investigation for improving ceramic production technologies entails the use of inexpensive local materials. On the one hand, this contributes to a decrease in the consumption of electricity and materials, and on the other hand, calls for studying the physicochemical processes which take place in using nontraditional components.

The current trend is to expand the use of calcium-containing materials in ceramic mixtures, since they can be used to produce ceramic articles, primarily faience articles, whose properties meet the prescribed specifications [1 – 3].

The less expensive calcium-bearing materials (chalk, marble, limestone, dolomite) are naturally abundant and act as the second kind fluxes in ceramic production at firing temperatures above 1000°C. The efficiency of their use at lower temperatures depends on several factors. First, solid-phase reactions play a significant role in crystalline mixtures in low-temperatures sintering. Second, the formation of certain compounds in the course of solid-phase reactions proceeds with a certain ratio of mixture components. The principal mineral-forming reactions occur at higher temperatures, but calcium-bearing mixtures with a certain component ratio within the temperature interval of 900 – 1000°C produce various calcium-containing compounds. Many researchers note the efficiency of the formation of calcium aluminate of the anorthite type in the ceramic crock with an increased content of calcites [3, 4].

The results of the studies revealed that anorthite in low-temperature firing is formed with a certain quantitative ratio of alkaline-earth and alkaline components. Since the alkaline oxides in low-temperature and predominantly solid-phase sintering act as mineralizing and activating additives, their content in the mixture should be limited and strictly determined. Their insignificant quantity facilitates the formation of thin liquid interlayers at granular boundaries, which increases the degree of contact between the reactant particles, the rate of the solid-phase reactions between them, and, consequently, the formation of the required crystal phase. If the amount of the liquid phase increases through an increased content of the alkaline components, CaO will partly dissolve in the excessive liquid phase, and the quantity of crystal phases formed with its participation will be significantly lower.

Solid-phase reactions are significantly affected by the activity of reactants, especially materials with a defective structure and, accordingly, with increased reacting capacity.

In this context, the use of calcium-containing wastes, which have greater reactivity, should yield positive results.

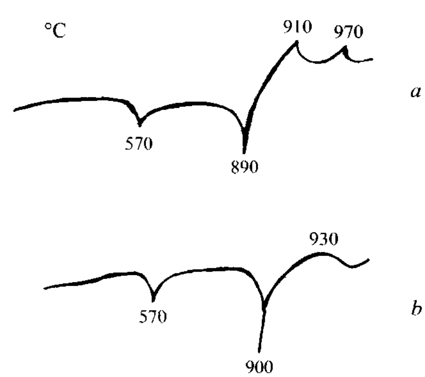

Fig. 1. DTA of ceramic mixture: *a*) RO : R_2O = 3.8 – 5.8; *b*) RO : : R_2O = 1.8 – 3.0.

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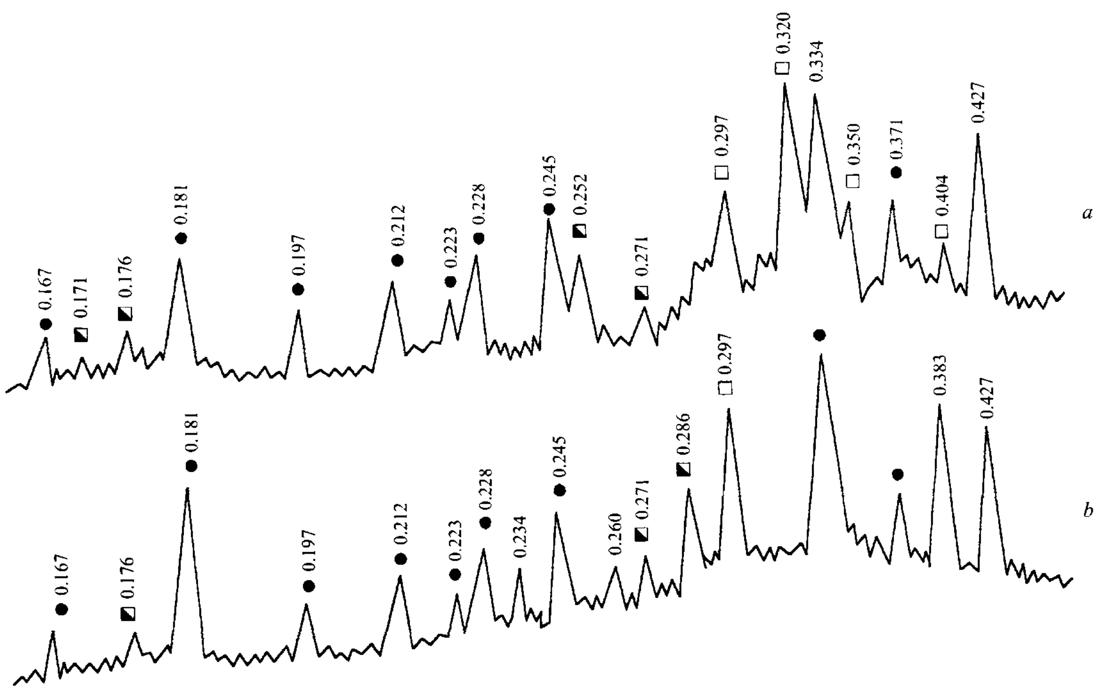

Fig. 2. X-ray pattern of ceramic crock: *a*) RO : R_2O = 3.8 – 5.8; *b*) RO : R_2O = 1.8 – 3.0; □) calcium aluminosilicates; ●) quartz; ◪) calcium silicates.

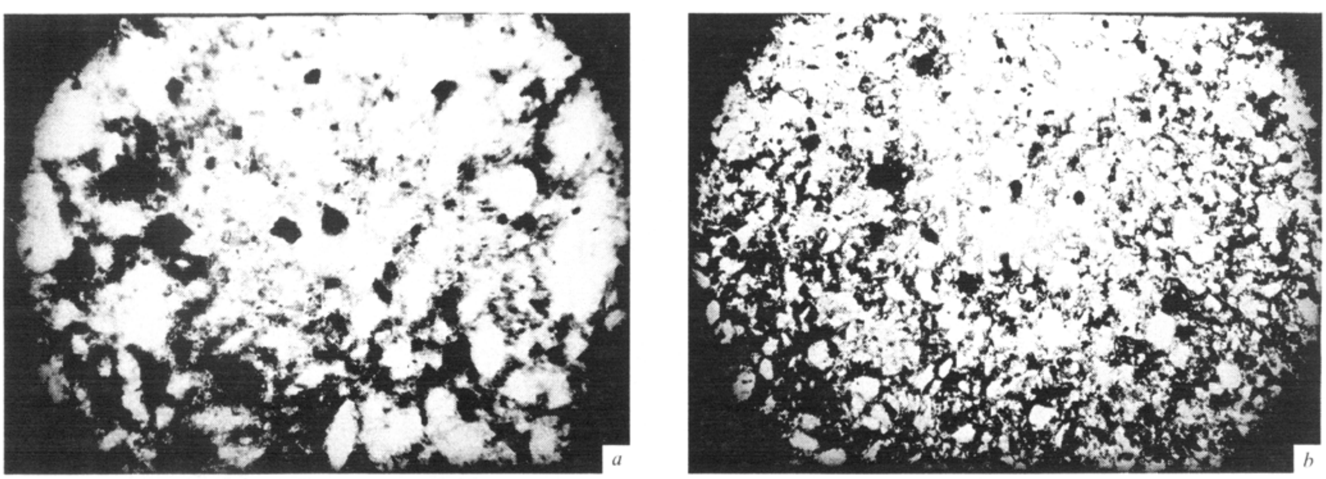

Fig. 3. Ceramic crock microstructure: *a*) RO : R_2O = 3.8 – 5.8; *b*) RO : R_2O = 1.8 – 3.0.

The present study involved mine water purification wastes which contained up to 50% CaO and whose crystal lattice had a defective structure, which was found as a result of physicochemical studies.

This material was used as a basis for ceramic mixtures for facing tiles, whose properties meet the requirements of GOST 6141–91. The water absorption of the mixtures based on polymineral clays and carbonate materials does not exceed 24% (Russian Federation patent 2065424).

With the object of intensifying the sintering process and the formation of the crock structure with required service properties, mixtures with various ratios of alkaline and alkaline-earth components and a constant weight content of highly calciferous waste (20%) were investigated. The ratio RO : R_2O varied from 3.4 to 5.8 and from 1.6 to 3.0 depending on the alkaline component content, and the emerging structures differed significantly.

With the ratio RO : R_2O equal to 3.4 – 5.8, i.e., with a low content of alkaline components, thermographic analysis identified the formation of a crystal phase with a highly intense exothermic effect within the temperature interval of

$890 - 920°C$ (Fig. 1*a*). The mixtures with the $RO:R_2O$ ratio equal to $1.6 - 3.0$ which contained a substantial amount of alkaline metal oxides did not exhibit perceptible exothermic peaks corresponding to the crystallization process in low-temperature firing in the interval of $900 - 950°C$ (Fig. 1*b*).

These results are supported by the x-ray phase analysis data (Fig. 2). As can be seen, the main crystal phase in the crock structure with $RO : R_2O = 3.4 - 5.8$ is anorthite $CaO \cdot Al_2O_3 \cdot 2SiO_2$ (0.404, 0.320, 0.319 nm). The samples with $RO : R_2O = 1.8 - 3.0$ are significantly different in the fact that they mainly exhibit the crystallization of calcium orthosilicate with a simple insular structure which is easily formed in the presence of a substantial amount of liquid phase, and calcium aluminosilicate.

The ratios of the crystallizing phases, as well as the quantitative ratios of the crystal and vitreous phases, were investigated in more detail by the petrographic method on clear sections in reflected and polarized light (Fig. 3).

The structure of the samples represents close-grained agglomerate consisting of crystal phases with grains of various shapes not more than 0.15 μm in size and a vitreous phase with numerous crystalline inclusions. The emerging structures have significantly different ratios of the crystal and the vitreous phases.

Thus, the crock structure with the ratio $RO : R_2O$ equal to $3.8 - 5.8$ is predominantly crystalline with a low content of the vitreous phase: up to 15%. With a high content of alkaline oxides, the vitreous phase content increases up to 40 – 45%, which has a perceptible effect on the liquid-phase sintering process and the crock structure formation.

The obtained results indicate that the predominant process in low-temperature sintering with $RO : R_2O = 3.8 - 5.8$ is solid-phase sintering with the formation of a coarse-crystal phase of the anorthite type with a grain density of 2.97 g/cm^3, which facilitates the formation of a crock structure with well developed sealed porosity and low shrinkage. An increase in the liquid phase content determines the formation of calcium silicates, which, together with the vitreous phase, provide for a sufficiently dense crock structure with substantial firing shrinkage.

Thus, the performed studies clarified the sintering specifics of ceramic mixtures based on highly calciferous waste and determined the optimum content of alkaline and alkaline-earth components, which opens wide possibilities in utilization of industrial waste and the development of efficient ceramic production technologies.

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